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ACTINIC ELECTROLYSIS

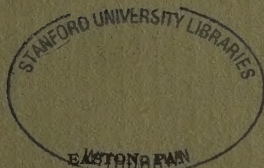
A THESIS

SUBMITTED TO THE UNIVERSITY FACULTY OF CORNELL UNIVERSITY
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

BY

CARL GEORGE SCHLUEDERBERG

1908



ESCHENBACH PRINTING COMPANY

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Action of Ferric Sulphate on Copper in Darkness and in Light

The following series of experiments were carried out for the purpose of determining whether any difference exists in the rates of action of ferric sulphate on copper in darkness and in light.

For this purpose pure copper was made up into a shape similar to an ordinary rotating platinum anode. Several of these copper test pieces were prepared, each of about 20 grams weight. In each experiment 300 cc of a solution of ferric sulphate of known strength was used; the copper test piece was suspended to a certain depth of solution and rotated by means of a small electric motor.

An ordinary photographic dark room was used for one set of experiments and October-November sunlight for the other set.

Most of the experiments were carried out at room temperature and in order that parallel experiments should be conducted at the same temperature, it was usually necessary to carry out the "Sunlight" experiments with the beaker of ferric sulphate solution immersed in a larger beaker of water to which ice could be added when necessary.

The following factors entered into these experiments:

- (1) Time.
- (2) Concentration of solution.
- (3) Temperature of solution.
- (4) Speed of rotation of metal test piece.
- (5) Surface of metal.
- (6) Volume of solution.
- (7) Illumination.

The factors No. 1 and No. 2 were varied at will, and in a few instances, factor No. 3. Factors No. 4, No. 5 and No. 6 were kept as constant as possible. In the case of factor No. 7 the experiments were mostly carried out in pairs under identi-

cal conditions except that one was in total darkness and the other in the brightest obtainable sunlight.

Experiments No. 1 and No. 2

Fifty grams of ferric sulphate in 300 cc of water.
 Time = 460 minutes.
 Temperature = 30°.
 Copper dissolved in light = 5.0459 grams.
 Copper dissolved in darkness = 6.0749 grams.
 Difference¹ = — 1.0290 grams.

Owing to the large amount of copper dissolved in the above experiment, amounting to about 25 percent of the total weight of the test piece, it was decided to cut down the time and the concentration.

Experiments No. 3 and No. 4

Thirty grams of ferric sulphate in 300 cc of water.
 Time = 330 minutes.
 Temperature = 30°.
 Copper dissolved in light = 3.1270 grams.
 Copper dissolved in darkness = 3.1516 grams.
 Difference = — 0.0246 gram.

As the amount of copper dissolved was still too large the time and concentration were again reduced.

Experiments No. 5 and No. 6

Ten grams of ferric sulphate in 300 cc of water.
 Time = 190 minutes.
 Temperature = 30°.
 Copper dissolved in light = 0.9981 gram.
 Copper dissolved in darkness = 1.0263 grams.
 Difference = — 0.0282 gram.

These experiments were immediately (same day) repeated at the temperature of melting ice with the following results:

¹ The difference is marked + when the copper dissolved in light exceeds that in darkness, and — when the amount dissolved in darkness exceeds that dissolved in light.

Experiments No. 7 and No. 8

Ten grams of ferric sulphate in 300 cc of water.

Time = 190 minutes.

Temperature = Melting Ice.

Copper dissolved in light = 0.9828 gram.

Copper dissolved in darkness = 0.9483 gram.

Difference = + 0.0345 gram.

From the above results it is seen that the difference in temperature of 30° makes practically no difference in the amount of copper dissolved. Also the reaction in light is not appreciably different from that in darkness.

In the following pair of experiments the time was kept the same as before and the concentration of the ferric sulphate solution reduced to one-quarter that of the experiments immediately preceding. It is worthy of note that the copper dissolved is about one-fourth that of the preceding experiments, No. 5, No. 6, No. 7 and No. 8.

Experiments No. 9 and No. 10

2.5 grams of ferric sulphate in 300 cc of water.

Time = 190 minutes.

Temperature = 25° .

Copper dissolved in light = 0.2651 gram.

Copper dissolved in darkness = 0.2610 gram.

Difference = + 0.0041 gram.

From this pair of experiments it would seem that the reaction went at the same rate in light as in darkness, yet the possibility still existed that the reaction had been allowed to run too far toward completion for any difference to be detected in the rate, or in other words, the time allowed was too great; hence, in the following experiments, the time was shortened considerably.

Experiments No. 11 and No. 12

Ten grams of ferric sulphate in 300 cc of water.

Time = 60 minutes.

Temperature = 25° .

Copper dissolved in light = 0.7384 gram.

Copper dissolved in darkness = 0.5347 gram.

Difference = + 0.2037 gram.

Apparently the reaction goes faster in the light, but the succeeding experiments show that this is not the case. The above difference is due to accidental variation in the speed of rotation of the metal.

Experiments No. 13 and No. 14

Ten grams of ferric sulphate in 300 cc of water.

Time = 40 minutes.

Temperature = 25°.

Copper dissolved in light = 0.6232 gram.

Copper dissolved in darkness = 0.6356 gram.

Difference = — 0.0124 gram.

Experiment 15

To test effect of speed, the same copper test piece as used in Experiment No. 14 was again rotated in darkness at a slightly lower speed under identical conditions with a loss in weight of only 0.5844 gram as against 0.6356 gram in Experiment No. 14, or a difference of 0.0512 gram of copper dissolved. Experiments No. 13 and No. 14 show practically no difference in the rate of the reaction in light and in darkness.

The differences in amounts of copper dissolved in light and darkness in Experiments No. 1, No. 2, No. 11 and No. 12 were due to accidental variation in speed of rotation. When the speed of rotation was the same in parallel experiments, practically no difference in amounts of metal dissolved in light or darkness could be detected.

Experiments No. 18 and No. 19

Ten grams of ferric sulphate in 300 cc of water.

Time = 60 minutes.

Temperature = 25°.

Copper dissolved in light = 0.9263 gram.

Copper dissolved in darkness = 0.9666 gram.

Difference = — 0.0403 gram.

In the next experiment the above time was cut in half.

Experiments No. 20 and No. 21

Ten grams of ferric sulphate in 300 cc of water.

Time = 30 minutes.

Temperature = 25° .

Copper dissolved in light = 0.6950 gram.

Copper dissolved in darkness = 0.6938 gram.

Difference = + 0.0012 gram.

This shows practically no difference in the rate in light and in darkness.

In the succeeding pair of experiments the concentration of solution was reduced to one-quarter that of the experiments immediately preceding and the time kept the same as in these experiments.

Experiments No. 22 and No. 23

2.5 grams of ferric sulphate in 300 cc of water.

Time = 30 minutes.

Temperature = 25° .

Copper dissolved in light = 0.1931 gram.

Copper dissolved in darkness = 0.1814 gram.

Difference = + 0.0117 gram.

In Experiments No. 24 and No. 25 the concentration of solution used in above experiments was cut in half.

Experiments No. 24 and No. 25

1.25 grams of ferric sulphate in 300 cc of water.

Time = 30 minutes.

Temperature = 25° .

Copper dissolved in light = 0.0923 gram.

Copper dissolved in darkness = 0.0910 gram.

Difference = + 0.0013 gram.

The above concentration of solution of ferric solution was cut in half.

Experiments No. 26 and No. 27

0.625 gram of ferric sulphate in 300 cc of water.

Time = 30 minutes.

Temperature = 25° .

Copper dissolved in light = 0.0488 gram.

Copper dissolved in darkness = 0.0458 gram.

Difference = + 0.0030 gram.

Experiments No. 28 and No. 29

1.25 grams of ferric sulphate in 300 cc of water.

Time = 30 minutes.

Temperature = 25°.

Copper dissolved in light = 0.0972 gram.

Copper dissolved in darkness = 0.1004 gram.

Difference = — 0.0032 gram.

The slight differences noticed in the four preceding pairs of experiments do not show any consistent variation in favor of light or darkness, nor are they of sufficient magnitude to indicate any such variation.

Considering the shortness of the run, the small amounts of copper dissolved and the impossibility of having the speed of the motor *exactly* the same under all conditions, the agreements are quite close.

Several experiments were carried out in which there was no stirring.

Experiments No. 30 and No. 31

2.5 grams of ferric sulphate in 300 cc of water.

Time = 190 minutes.

Temperature = 25°.

Copper dissolved in light = 0.0643 gram.

Copper dissolved in darkness = 0.0215 gram.

Difference = + 0.0428 gram.

This difference in the weight of copper dissolved is probably due to the natural circulation of the liquid in strong sunlight, for although the beaker was immersed in a larger beaker of ice water, it was impossible to keep all parts of the liquid at the same temperature for the sun shining down on the top layer of liquid would cause differences of temperature which would in turn induce some circulation of the liquid.

A fact worthy of particular note is the small amount of copper dissolved when there is no stirring. The test piece used in this case is exactly the same as that used in experiments where stirring took place.

Comparing with Experiments No. 9 and No. 10 in which the time and concentration of solution were the same as in this case, it is seen that 0.2610 gram of copper was dissolved

as against 0.0215 gram without the stirring. A difference of 1200 percent in favor of stirring.

Again in Experiments No. 22 and No. 23 with concentration of solution the same as above and time reduced to thirty minutes, or one-sixth of the above, the amount of copper dissolved with stirring exceeded that dissolved without stirring by 800 percent.

As a further test of the rate of solution of copper without stirring, two strips of copper identical in size were prepared and each placed on the bottom of a large beaker and covered with a moderate amount of solution. One beaker was placed in darkness and the other beaker immersed in a larger beaker of cold water and placed in moderate sunlight, the top of the beaker being carefully covered with a block of wood and light admitted through the sides only. In this way the temperature could be kept more nearly constant throughout the solution and diffusion largely prevented.

The weight of copper dissolved in each case was more nearly the same than in the preceding experiment, though evidently some diffusion did occur in the light.

Experiments No. 33 and No. 34

1.25 grams of ferric sulphate in 150 cc of water.

Time = 230 minutes.

Temperature = 25°.

Copper dissolved in light = 0.0628 gram.

Copper dissolved in darkness = 0.0567 gram.

Difference = + 0.0061 gram.

The reaction between copper and ferric sulphate may be expressed by the following equation: $\text{Cu} + \text{Fe}_2(\text{SO}_4)_3 = \text{CuSO}_4 + 2\text{FeSO}_4$.

The preceding experiments show that this reaction proceeds at the same rate in sunlight as in darkness, and they do not give any indication that the reaction is a photochemical one.

Noyes and Whitney¹ studied the rates of solution of solid substances in their own solutions. They say "the law govern-

¹ Noyes and Whitney: Jour. Am. Chem. Soc., 19, 930 (1897).

ing the rate of solution can be predicted with a considerable degree of probability; for the phenomenon may be considered as simply a process of diffusion. That is, we can imagine the sticks of solid substances surrounded by an indefinitely thin film of saturated solution, from which diffusion takes place into all portions of the solvent, this being kept homogeneous by rotation. If this were the case, the velocity of solution, in accordance with the law of diffusion, would be proportional to the difference between the concentration of the saturated solution and that of the solution present at the moment in question." They express the law as follows: "The rate at which a solid substance dissolves in its own solution is proportional to the difference between the concentration of that solution and the concentration of the saturated solution."

The question was further studied by Nernst¹ in an article entitled "Theory of Reaction Velocity in Non-Homogeneous Systems." In this article he takes the view that at the common surface of two phases equilibrium is established with great rapidity, and that the rate actually measured is that of diffusion throughout the liquid phase.

Thus, the principle, enunciated by Noyes and Whitney in connection with a physical change, is here applied to chemical and electrochemical reactions.

The case of the solution of magnesia in acids is cited, and it is assumed that the solution in immediate contact with the magnesia is saturated with the substance, and therefore slightly alkaline. Therefore, the rate of the reaction is simply that at which the acid diffuses to the common surface; if the acid is thoroughly stirred, the fall of concentration will be confined to a very thin layer surrounding the solid magnesia. For given conditions, this rate is constant and may be determined.

The same reasoning is applied to electrochemical cases where the common surface is that of the electrode. By

¹ Nernst: *Zeit. phys. Chem.*, **47**, 52 (1904).

keeping down the concentration the same formula may be applied as in purely chemical cases.

Erich Brunner¹ in an article entitled "Velocity of Reaction in Non-Homogeneous Systems" describes some experimental investigations of these theories. He derives a formula for the rate of solution of benzoic acid in water, which for a given rate of stirring and of temperature, involves the volume and the concentration of a saturated solution and successive values of the concentration of the dilute solution at a known interval of time. The rate of solution is found to bear a certain relation to the speed at which the stirring apparatus is revolved.

The velocity of reaction should be independent of the nature of the solid substance, provided that the concentration of the diffusing substance is practically zero at the surface of the solid.

In harmony with this it is found that the rates of solution of basic magnesium carbonate, magnesium hydroxide, and magnesium itself in benzoic acid are approximately equal. Magnesium and magnesium hydroxide dissolve equally rapidly in hydrochloric acid.

The velocity of electrolytic separation of hydrogen at a platinized platinum electrode from solutions of benzoic and hydrochloric acids containing an excess of potassium chloride, is, within certain limits, equal to the rate of solution of magnesium hydroxide.

Other reactions are studied which agree very well with the theory. A comparison of the rates of solution of magnesium hydroxide in different acids in the presence of their magnesium salts shows that they increase in the following series, benzoic, acetic, formic, hydrochloric, which order is the same as if these acids were arranged according to the magnitude of their diffusion coefficients.

My experiments, although they gave a negative result so far as any photochemical action is concerned, nevertheless

¹ Brunner: Zeit. phys. Chem., 47, 56 (1904).

furnish a striking example of the theory that the rates of many reactions are simply rates of diffusion and not rates of chemical reactions.

The reaction between copper and ferric sulphate is practically instantaneous and the observed rate depends entirely on the speed with which stirring is carried on. For instance, it is seen on comparing Experiments No. 9 and No. 10, which were carried out with stirring, with Experiments No. 30 and No. 31 in which the conditions were identical except for stirring, that about twelve times as much copper dissolved when there was an opportunity for diffusion of the copper sulphate and ferrous sulphate away from the surface of the copper, as in the case where no stirring occurred and the diffusion was consequently slower, especially in consideration of the fact that the absence of light would tend to prevent any natural diffusion. We know that, in the case of the electrolytic deposition of metals, the rate is only limited by the speed of rotation of the cathode.

In the same way it may be said that the rate of solution of a metal or substance is only limited by the mechanical possibility or difficulties of rotation of the specimen of metal or substance or of the stirring of the solution.

Thus, these results show that the reaction between copper and ferric sulphate is practically instantaneous and that, if there is anything of a photochemical nature above it, ordinary means of measurement will not detect it. They agree with and tend to confirm the work of Noyes and Whitney, Nernst and Brunner, already cited.

Electrolytic Chlorination of Acetic Acid, Benzene and Toluene

In the following sets of experiments the attempt is made to study the chlorination of several organic substances by electrolytic means and under varying conditions.

ACETIC ACID

Experiment 1.—Twenty grams of zinc chloride were dissolved in 300 cc of glacial acetic acid and electrolyzed in the

dark at 20° with platinum electrodes, the cathode being enclosed in parchment diaphragm electrodes, 11 × 1.5 cm.

It being impossible to get any current through the liquid at 100 volts pressure, water was gradually added up to about 25 cc. Current went to one-half ampere plus, and voltage dropped to 25 volts.

The solution became hot and some zinc, which had been deposited on the outside of the parchment diaphragm, was redissolved slowly by the liquid.

After one and one-quarter hours the current was shut off and 10 cc of the solution removed for analysis, as it was desired to determine the amount of halogen substituted in the acetic acid.

To get rid of any dissolved chlorides present in the portion pipetted off, silver nitrate was added in excess and the precipitated silver chloride was removed by filtration. Free chlorides having been thus removed, the filtrate was then boiled for some time in a flask with return condenser, thus hydrolyzing any chlor acetic acid which might be present and precipitating the chlorine as silver chloride which was collected on a Gooch filter and weighed in the usual manner.

Total silver chloride in 300 cc. liquid	= 0.09 gram.
Chlorine in 0.09 gram silver chloride	= 0.0223 gram.
1.25 hours × 0.5 amperes	= 0.625 amp. hrs.
0.625 ampere hours are equivalent to	= 0.825 gram Cl.
Chlorine available for substitution	= 0.412 gram.
Efficiency = $\frac{0.0223}{0.412} \times 100 = 5.42$ percent.	

Experiment 2.—200 grams of acetic acid, excess zinc chloride. Porous cup. Cathode same size as in Experiment 1 placed in cup. Anode about three times as large as in Experiment 1. Temperature = 0°. Electrolysis in the dark. Voltage 25 at first, rapidly fell to 7 volts. Analysis same as before.

Total silver chloride in 200 cc	= 0.2340 gram.
Chlorine in 0.2340 gram AgCl	= 0.0578 gram.
Five hours $\times$ 0.25 ampere	= 1.25 amp. hrs
1.25 ampere hours equivalent to	= 1.65 grams Cl.
Chlorine available	= 0.82 gram.
Efficiency	= 7.05 percent.

From this experiment it is seen that lowering the anode current density and diminishing the temperature of the solution has resulted in but a very slight increase in efficiency.

Experiment 3.—Same as Experiment 2, except that a platinum wire was used for anode in order to try effect of increase in current density at anode.

Voltage 110	Analyzed 10 cc portion
Total silver chloride in 200 cc	= 0.4480 gram.
Chlorine in 0.448 gram AgCl	= 0.1110 gram.
Fifteen hours $\times$ 0.2 amperes	= 3.00 amp. hrs.
3.00 ampere hours equivalent to	= 3.96 grams Cl.
Chlorine available	= 1.98 grams.
Efficiency	= 5.6 percent.

Using wire anode and consequently high current density did not give a better yield of substituted acetic acid.

Experiment 4.—A repetition of Experiment 2 gave equally unsatisfactory results, although the time of the electrolysis was extended over about 20 hours. Efficiency about 1 percent.

Due to the poor conductivity of acetic acid, even with zinc chloride dissolved in it, a high voltage across the terminals of the cell was necessary in order to force an appreciable current through the electrolyte. On account of the consequently large potential gradient in the electrolyte, metallic zinc was usually deposited on the surface of the diaphragm surrounding the cathode. (Electrostenolysis).

As this zinc gradually dissolved, giving off bubbles of gas, it would seem that it reacted with a larger part of the chlor acetic acid formed, reducing same with the formation of zinc chloride and the evolution of hydrogen.

Possibly this accounts for the poor yield of substituted acetic acid, especially in Experiment 3 where the time was

lengthened out to twenty hours, thus giving ample opportunity for the deposited zinc to react on the solution. If the above explanation is correct obviously no matter how the time of the run might be extended, the results would be equally unsatisfactory.

As a test experiment, metallic zinc was treated with mono-chlor acetic acid. The metal dissolved slowly and the resulting solution gave a precipitate with silver nitrate, thereby showing the formation of zinc chloride and the destruction of the chlor acetic acid.

Experiment 5.—In order to overcome trouble caused by the precipitated zinc reducing the chlor acetic acid dry hydrogen chloride was passed into glacial acetic acid for one hour.

A portion of the acid on addition of silver nitrate gave precipitate of silver chloride, showing the absorption of some of the hydrogen chloride by the acetic acid. This was electrolyzed for five hours under conditions similar to Experiment 4. Voltage 110, current 0.2 ampere at start gradually fell to below 0.1 ampere. On analysis only a trace of substituted acid was obtained.

Evidently the amount of hydrogen chloride absorbed was very small and hence the lack of satisfactory results.

Experiment 6.—In this experiment use was made of an H tube in order to protect the chlor acetic acid from being acted on by the zinc by confining it to one arm of the H and the zinc to the other. The wire anode was placed in one arm of the H and the platinum strip cathode in the other arm. The two arms of the H were of course closed at the lower ends. In this was placed 80 cc of acetic acid saturated with zinc chloride.

Temperature = 20°,—Diffused light.

Weight AgCl in 10 cc	=	0.0350 gram.
Total AgCl in 80 cc	=	0.2800 gram.
Chlorine in 0.2800 gram AgCl	=	0.0693 gram.
Twenty-seven hours $\times$ 30 milliamperes	=	0.810 amp. hrs.
0.810 amp. hrs. equivalent to	=	1.07 grams Cl.
Chlorine available	=	0.535 gram.
Efficiency	=	12.9 percent.

Evidently from the higher efficiency obtained, this procedure partially overcomes the reduction of the chlor acetic acid by the precipitated zinc, as free circulation of the electrolyte is prevented, and by having the cathode arm of the H shorter than the other arm, a large part of the acid does not come into contact with the cathode. However, the efficiency is still very low, making the electrolytic chlorination unsatisfactory.

Experiment 7.—One hundred cc of glacial acetic acid was mixed with 10 cc of concentrated hydrochloric acid and electrolyzed at room temperature—20°—in very diffused light. Voltage 15.

Ten cc taken for analysis.

Weight of silver chloride obtained	= 0.0220 gram.
Total silver chloride in 110 cc	= 0.2420 gram.
Chlorine in 0.242 gram AgCl	= 0.0600 gram.
Ten hours — 0.2 ampere	= 2 amp. hrs.
Two ampere hours equivalent to	= 2.64 grams Cl.
Chlorine available	= 1.32 grams.
Efficiency	= 4.55 percent.

Hydrochloric acid, as a source of chlorine, does not give any better efficiency than obtained in the previous experiments with zinc chloride. Anhydrous hydrochloric acid, were it sufficiently soluble in acetic acid, would probably work much better than the ordinary concentrated acid which, of course, introduces considerable water.

Experiment 8.—Two hundred cc of glacial acetic acid was placed in a liter bottle in which was 3.4 grams of platinum black and platinum foil. Room temperature = 20°. Acid was saturated with chlorine and bottle filled with same, then stoppered and placed in a dark cupboard.

Started, December 10, 1906.

Finished, May 13, 1908.

Elapsed time, 5 months.

Analysis of 10 cc portion gave:

Weight of silver chloride	= 0.0123 gram.
Total silver chloride in 200 cc	= 0.2460 gram.
Total chlorine	= 0.0610 gram.
Corresponds to 0.1625 gram of CH_2ClCOOH .	

The amount of substitution taking place under these conditions is very small indeed, especially when the fact that the experiment extended over 5 months time is taken into consideration.

From the foregoing series of experiments it is evident that, while it is possible to chlorinate acetic acid electrolytically, yet from the standpoint of efficiency, the results obtained are of a very unsatisfactory nature.

In the first place, glacial acetic acid, even when saturated with zinc chloride, is such a poor conductor as to make it impossible to get an appreciable current through it with 110 volts pressure.

With ordinary acetic acid an appreciable current can be gotten through at this voltage, but the potential gradient is very high and metallic zinc is deposited on the diaphragm, which causes decomposition of the chlor acetic acid and cuts down the yield; but even when this trouble is eliminated the efficiency is still too low.

Neither variations in temperature from that of melting ice to ordinary room temperature, nor variations in the anode current density seem to make an appreciable difference in the efficiency.

In the beginning of this work it was postulated (1) that light causes a dissociation, (2) dissociation effects of light can be duplicated electrolytically, (3) when light and halogen carriers act in the same way, the results can be duplicated electrolytically.

The ordinary chemical chlorination of compounds of the type of acetic acid is best carried out in sunlight, and in the presence of certain carriers, such as phosphorus.

It was thought that the chlorine obtained electrolytically, and ordinary chlorine, in the presence of sunlight, would act in the same manner; but it has since been found in the chlorination of toluene that these two kinds of chlorine act differently. In toluene, electrolytic chlorine substituted in the ring, and ordinary chlorine, in the presence of sunlight, in the side chain. Thus, it would seem that the hydrogen in acetic

acid, which is substituted by chlorine in the sunlight, is of the same kind as that in the side chain of toluene. This chlorine is designated as positive in distinction to the ring chlorine of toluene or benzene which is called negative.

It has been assumed that light causes a dissociation of chlorine into positive and negative chlorine.¹

When acetic acid is chlorinated in sunlight the positive chlorine can be considered as displacing the hydrogen of the acid, which subsequently unites with the remaining negative chlorine to form hydrogen chloride.

Postulate No. 2 that the dissociation effects of light can be duplicated electrolytically, therefore does not hold.

Postulate No. 3, as it reads, does not hold, but then only a few carriers act in the same way as light, among them phosphorus. When a carrier acts in a different sense from light, its action can be duplicated electrolytically.

An ordinary carrier, such as ferric chloride, can be considered as dissociating into ferrous chloride and negative chlorine. The action of such a carrier can be duplicated electrolytically. With phosphorus pentachloride, dissociation may occur into phosphorus trichloride and positive chlorine, thus acting in the same sense as light.

Since in all cases in the electrolytic chlorination of acetic acid the efficiency obtained was extremely low, it is safe to assume that what chlorination did occur, was due to ordinary chlorine gas discharged from the electrode and dissolved in the acid, and not to the negative chlorine as set free from the anode.

Chlorination of Benzene

The electrolytic chlorination of benzene was studied under varying conditions and with several sources of chlorine.

In these first experiments, as a source of chlorine, ether was saturated with zinc chloride and then added to the benzene about to be electrolyzed. The total chlorine was determined with alcohol and excess of sodium according to the method of

¹ Bancroft: *Jour. Phys. Chem.*, **12**, 439 (1908).

Stephanow.¹ By subtracting the free chlorides obtained by direct precipitation with silver nitrate, the substituted chlorine was obtained.

Experiment 1.—A mixture of 80 cc of benzene and 80 cc of ether saturated with zinc chloride was electrolyzed at 25° with porous cup and platinum electrodes. 110 volts, dark.

Total silver chloride	= 0.7984 gram.
Total chlorine	= 0.1970 gram.
Fifteen hours $\times$ 25 M. A.	= 0.375 amp. hrs.
0.375 ampere hours equivalent to	= 0.495 grams Cl.
Chlorine available	= 0.247 gram.
Efficiency	= 80.0 percent.

Experiment 2.—Electrolyzed a mixture of 60 cc of benzene and 75 cc of ether saturated with zinc chloride. Porous cup, dark, temperature = 25°, platinum electrodes 1.5 $\times$ 12 cm, volts = 100.

Total silver chloride	= 0.7260 gram.
Total chlorine	= 0.180 gram.
Twenty-four hours $\times$ 15 M. A.	= 0.360 amp. hrs.
0.360 amp. hrs. equivalent to	= 0.475 gram Cl.
Chlorine available	= 0.237 gram.
Efficiency	= 76.0 percent.

Experiment 3.—The chlorination of benzene was next tried, using as a source of chlorine a solution of sodium chloride, sulphuric acid and water.² The advantage of this solution is that it will absorb very little chlorine.

A Classen dish and rotating anode were used, the anode being arranged so as to be entirely in the upper or benzene portion of the solution. Seventy-five cc of Oettel solution and 75 cc of benzene were used. Temperature = 0°.

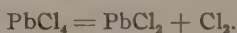
Total silver chloride	= 0.2600 gram.
Total chlorine	= 0.0643 gram.
Two hours $\times$ 2 amperes	= 4.0 amp. hrs.
4 ampere hours equivalent to	= 5.28 grams Cl.
Chlorine available	= 2.64 grams Cl.
Efficiency	= 2.29 percent.

¹ Stephanow: Ber. chem. Ges., Berlin, 39, 4056 (1906).

² Felix Oettel: Zeit. Elektrochemie, 2, 58 (1895), 160 grams NaCl, 140 grams H₂SO₄, made up to a liter with water.

Efficiency obtained with this arrangement is very low, possibly due to the temperature or to the electrolyte and high current density. As the other methods of electrolytic chlorination gave satisfactory results, the causes of the poor efficiency obtained in this experiment were not investigated further at the time.

Experiment 4.—From the preceding three experiments it is seen that chlorine when set free at the anode of an electrolytic cell will substitute in the benzene ring. In this connection the question came up as to what would be the action of chlorine on the benzene ring when obtained from another source, such as an instable chlorine compound. Lead tetrachloride was prepared and used as a source of chlorine. This compound, being of a very instable nature, beaks down on introduction into benzene, giving off two chlorine atoms and forming insoluble lead chloride.



Twenty cc of cold benzene were treated with 3.5 grams of lead tetrachloride, added a drop at a time, in darkness. The odor of hydrochloric acid was noticeable and the benzene turned a beautiful red color, which, however, disappeared after about an hour's time leaving a clear solution with a white precipitate of lead chloride at the bottom of the beaker. A certain amount of white precipitate was formed, together with the red color of the solution, immediately the first drop of lead tetrachloride was added.

Total silver chloride	= 0.3860 gram.
Chlorine	= 0.0958 gram.
3.5 grams PbCl_4 equivalent to	= 0.7120 gram Cl_2 .
Chlorine available	= 0.356 gram.
Efficiency	= 26.9 percent.

Experiment 5.—Twenty-five cc of benzene treated with 6 grams of lead tetrachloride, cold, dark.

Total silver chloride	= 1.4895 grams.
Chlorine	= 0.368 gram.
Six grams PbCl_4 equivalent to	= 0.122 gram Cl_2 .
Chlorine available	= 0.61 gram.
Efficiency	= 60.4 percent.

From the above experiments it is seen that chlorine from an instable compound of chlorine will substitute in the benzene ring.

The larger quantity of lead tetrachloride used in Experiment 5 may account for the increase in efficiency over Experiment 4.

From the foregoing experiments it is seen that electrolytic chlorine will replace hydrogen in the benzene ring. Again, chlorine from the decomposition of lead tetrachloride replaces the hydrogen of the ring in a similar manner. It is known that when chlorine is passed into benzene in the presence of a carrier such as ferric chloride, substitution takes place. Thus, the final result is the same with electrolytic chlorine, as that from an instable chlor compound, or chlorine in the presence of a carrier such as ferric chloride.

In an article on halogen carriers Lothar Meyer¹ considered that in the chlorination of benzene in the presence of ferric chloride, an addition compound is first formed between the benzene and the ferric chloride. This compound, in the presence of free chlorine, then breaks down, whereupon the chlorine of the carrier unites with the hydrogen of the benzene forming hydrogen chloride, and each is replaced by an atom of the free chlorine. In the same way, if benzene were being brominated with ferric chloride as a carrier, hydrogen chloride would first be formed and then the free bromine would substitute in the ring and in the carrier. According to this theory, substitution in the ring takes place subsequent to the formation of hydrogen chloride.

On the basis of this theory of Lothar Meyer's, the formation of chlorobromobenzene compounds in the bromination of benzene, with ferric chloride as a carrier, would be out of the question, nor does he speak of having obtained any such compounds in the course of his work. However, an article appeared a few years later which places the subject in quite a different light.

¹ L. Meyer: Jour. prakt. Chem., 142, 502 (1886).

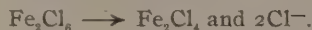
MacKerrow,¹ in studying bromine carriers, used ferric chloride as a carrier in the bromination of several nitrobenzenes. In a number of cases he found that chlorine substituted along with the bromine, giving compounds such as chloropentabromobenzene, dichlorotetrabromobenzene and tetrachlorodibromobenzene.

If, however, as Meyer claims, substitution takes place subsequent to the formation of hydrogen chloride, it would be hard to account for the fact that MacKerrow found the chlorine from the ferric chloride substituted in the benzene ring instead of being evolved as hydrogen chloride.

In view of these facts, it would seem that the action of the carrier can be explained in a manner more nearly correct by assuming that the chlorine of the ferric chloride, which may be designated as negative chlorine, displaces the hydrogen of the ring, which may also be considered as negative in character, thus forming a chlor-benzene.

Subsequently, this hydrogen unites with other chlorine from ferric chloride and is evolved as hydrogen chloride or in the case of bromination, as hydrogen bromide. The carrier which has been thus deprived of part of its chlorine combines with any free halogen present, say bromine, and forms a ferric chlor bromide. This, in turn, can act as a carrier just as before, causing more halogen to substitute in the ring and it may be converted finally into ferric bromide.

When acting as a carrier, ferric chloride may be looked upon as dissociating into ferrous chloride and negative chlorine, according to the following equation



Part of the negative chlorine obtained from the ferric chloride may then displace some of the hydrogen of the benzene ring, which is also considered to be negative in character, thus forming chlorbenzene. Subsequently this hydrogen unites with the remaining negative chlorine, forming hydrogen chloride.

¹ MacKerrow: Ber. chem. Ges., Berlin, 24, 2939 (1891).

In the presence of free chlorine, the ferrous chloride is changed to ferric chloride, in which condition it is ready to again act as a carrier.

When acting as a carrier in the bromination of benzene, a compound such as $\text{Fe}_2\text{Cl}_4\text{Br}_2$ may be formed, which in turn, may give up more chlorine to the benzene and be converted finally to ferric bromide, or what seems more probable, the hydrobromic acid split off may react with a compound such as $\text{Fe}_2\text{Cl}_4\text{Br}_2$ reducing it to ferric bromide and evolving hydrogen chloride.

This is substantiated by the fact, that ferric chloride when used as a carrier in the bromination of benzene is converted to ferric bromide.¹ This theory accounts for the formation of chlorobromobenzenes when ferric chloride is used as a carrier in the bromination of benzene, which compounds cannot be accounted for on the basis of the assumption made by Lothar Meyer.

In the same manner, it may be assumed that the negative electrolytic chlorine displaces the hydrogen of the ring and the chlorine from lead tetrachloride, which may be considered as negative, acts in the same way. The theory also accounts for the reaction velocity, in the case of ferric chloride, benzene, and chlorine, being found proportional to the first power of the concentration of the ferric chloride.²

MacKerrow also studied the action of ferric chloride, alone, on dinitrobenzene. He heated the mixture to a very high temperature and in one case an explosion occurred, and on a second trial a complete breakdown took place, giving some hydrogen chloride and ferrous chloride in addition to other products.

Page,³ in studying inorganic chlorides as chlorine carriers, tried the experiment of heating ferric chloride with benzene in a sealed tube a temperature of 100° . On opening the tube there was no evidence of any gas pressure. A part of the

¹ Meyer and Scheufelen: *Liebig's Ann.*, 231, 164 (1885).

² Slator: *Jour. Chem. Soc.*, 83, 729 (1903).

³ Page: *Liebig's Ann.*, 225, 205 (1884).

benzene was charred and formed a black bituminous mass with the ferric chloride. He was not able to detect ferrous salt either in the liquid or in the residue. From this he concludes that ferric chloride, when acting as a carrier, cannot, by giving up its chlorine to the ring compound, be reduced to ferrous chloride and be changed back again to ferric chloride. He then proceeds to build up a theory of addition products similar to the one cited in this paper under Lothar Meyer's work.

Now, if it could be shown that ferric chloride alone will react with benzene, considerable support would be extended to the theory that the chlorine of the carrier displaces the hydrogen of the benzene and that subsequently hydrogen chloride is formed. With this in mind the following experiments were performed.

Experiment 6.—In this experiment 65 cc of benzene were mixed with 12 grams of pure anhydrous ferric chloride in a round bottom flask fitted with a return condenser. This was exposed to bright sunlight for four hours and occasionally heated with a Bunsen burner. A brisk reaction took place, lasting considerable time after each heating, apparently evolving considerable heat, as the liquid was kept at the boiling point for some ten minutes or more in each instance. The odor of hydrochloric acid could be detected at the top of the return condenser and moist litmus paper gave test for acid. At the end of the above-mentioned time, the supernatant liquid, after being allowed to cool, was poured off. This had a decided deep brown color. With a hard filter and suction this liquid was obtained as a clear brownish yellow oil.

On analysis of a 10 cc portion, the following results were obtained:

Substitution	= 0.0425 gram AgCl.
Total silver chloride	= 0.2762 gram AgCl.
Total chlorine	= 0.0684 gram Cl.
Equivalent to	= 0.227 gram C_6H_5Cl .

The brown supernatant liquid when added to potassium ferricyanide gave a blue color (Turnbull's blue), thus indicating the presence of iron in the ferrous condition.

This experiment shows that it is possible to chlorinate benzene with a chlorine carrier, "ferric chloride," in the absence of free chlorine, provided the experiment be carried out in the sunlight and at a sufficiently high temperature to start the reaction and cause it to proceed at a fairly rapid rate, but not so hot as to cause a breakdown.

The lack of success of Page and other experimenters in this line is probably accounted for by the fact that they failed to carry out the experiment in sunlight and also heated to too high a temperature.

Thus it is seen that electrolytic chlorine which may be considered as negative; chlorine from an instable compound, such as lead tetrachloride, which may also be considered as negative, and chlorine from ferric chloride, also negative, all react with benzene in a similar and consistent manner. These facts are satisfactorily accounted for by the theory that the negative hydrogen of the benzene ring is displaced by negative chlorine and that it subsequently forms hydrogen chloride.

ADDITION PRODUCTS.

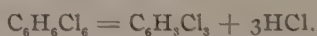
As a matter of interest the action of gaseous chlorine on benzene in the presence of dilute sodium hydroxide solution, and then in the presence of water, was studied with the object of determining the amount of addition and substitution products formed in each case.

Mathews¹ makes the statement that the formation of chlorine addition products of benzene proceeds best in the presence of a very dilute solution of sodium hydroxide and *almost* as well within the presence of water. No figures are given comparing the relative amounts of benzene hexachloride formed in the two cases, nor were any experiments made to determine whether any substitution products were

¹ Mathews: Jour. Chem. Soc., 59, 166 (1891).

formed when the chlorination was carried out in the presence of water or any other solution, though the possibility of the formation of substitution compounds is mentioned.

The total chlorine was determined by sodium, alcohol, and precipitation as silver chloride—method of Stephanow. The addition chlorine was determined by boiling the oil with alcoholic caustic soda, precipitating the chlorine as silver chloride and multiplying the result by 2 as in this method only half the chlorine is split off.



Experiment 7.—In an ordinary gas wash bottle were placed 100 cc of benzene and 75 cc of a 1 percent solution of sodium hydroxide. This was placed in very diffused light and at room temperature—20°—chlorine gas bubbled in at a fairly rapid rate for one and one-half hours. The gas passed first into the hydroxide solution and from there to the upper layer of benzene where it was absorbed. The benzene took on a yellow color and in some cases a portion of it fell to the bottom of the bottle due to the increase of specific gravity consequent to the absorption of chlorine. During the passage of chlorine into the benzene an increase of temperature was noticed.

Before analysis the benzene was washed repeatedly in a separatory funnel to eliminate all free chlorine.

Analysis of 5 cc portions gave

Total chlorine	2.2610 grams AgCl.
Addition chlorine	2.2680 grams AgCl.
Percent addition	100 percent.

Evidently in this case all the chlorine goes to form benzene hexachloride.

Experiment 8.—One hundred cc of benzene, 75 cc of water in gas wash bottle. Chlorine passed in for one and one-half hours, room temperature, 20°, very diffused light. Benzene turned yellow in color, same as in Experiment 6, and slight increase in temperature was noticed.

Analysis of 5 cc portions gave

Total chlorine	= 2.3376 grams AgCl.
Addition chlorine	= 2.2664 grams AgCl.
Difference	= 0.0712 gram AgCl.
Percent addition	= 96.8 percent.
Percent substitution	= 3.2 percent.

The results of these experiments show that with dilute caustic solution all the chlorine goes to form addition products while when pure water was used some substituted benzene was formed as well as benzene hexachloride.

Chlorination of Toluene

A study of the chlorination of toluene under varying conditions was next taken up.

Experiment 1.—In a Classen dish with rotary platinum anode were placed 100 cc of toluene and 175 cc of an Oettel solution. Very diffused light, temperature of melting ice.

Total silver chloride	= 1.3070 grams.
Side chain silver chloride	= 0.3125 gram.
Ring silver chloride, difference	= 0.9945 gram.
Total chlorine	= 0.3235 gram.
Six hours $\times$ 2 amperes	= 12.0 amp. hrs.
12 ampere hours equivalent to	= 15.86 grams Cl.
Chlorine available	= 7.93 grams.
Efficiency	= 4.07 percent.
Percentage ring	= 76.1 percent.
Percentage chain	= 23.9 percent.

Experiment 2.—Same as Experiment 1, except that the time of the electrolysis was reduced to five hours instead of six hours and the experiment was carried out in total darkness.

Total silver chloride	= 1.8225 grams.
Side chain silver chloride	= 0.4270 gram.
Ring silver chloride	= 1.3955 grams.
Total chlorine	= 0.4510 gram.
Five hours $\times$ 2 amperes	= 10.0 amp. hrs.
10 ampere hours equivalent to	= 13.22 grams Cl.
Chlorine available	= 6.61 grams.
Efficiency	= 6.82 percent.
Percentage ring	= 76.6 percent.
Percentage chain	= 23.4 percent.

It is worthy of note that these two experiments check each other quite well as regards the percentage of chlorine

in side chain and in ring. The slight difference in efficiency may be due to the anode being farther from the lower layer of Oettel solution and more exposed to the toluene.

Chlorination of Toluene at Low Current Density

Experiment 3.—Seventy-five cc of toluene and 100 cc Oettel solution in Classen dish, rotating platinum anode, temperature melting ice, very diffused light.

Total silver chloride	= 1.3764 grams.
Side chain silver chloride	= 0.0552 gram.
Ring silver chloride	= 1.3212 grams.
Total chlorine	= 0.3405 gram.
Fifteen hours $\times$ 0.09 ampere	= 1.35 amp. hrs.
1.35 amp. hours equivalent to	= 1.78 grams Cl.
Chlorine available	= 0.89 gram.
Efficiency	= 38.25 percent.
Percentage ring	= 95.98 percent.
Percentage chain	= 4.02 percent.

From the results obtained in this experiment it would seem that, by lowering the current density, the percentage substitution in the ring is increased and that of the side chain reduced to a very small figure. Also, the total efficiency is much higher than before.

Electrolytic Chlorination of Boiling Toluene

Experiment 4.—For this experiment a wide-mouth pear-shaped flask was fitted with a return condenser and platinum electrode, the cathode being a strip of platinum, 1.5 $\times$ 12 cm., doubled on itself and covering the bottom of the flask. The anode was of the regulation rotating type. During the course of a run the cathode was completely immersed in the lower liquid layer which was the source of chlorine. The cathode was connected to a short platinum wire sealed into a bent glass tube which extended from the bottom of the flask through the cork. The shank of the anode was sealed into a glass tube passing through the cork in such a manner that by sliding same up or down, or by twisting, the position of the anode could be adjusted as desired. The flask was rested on a sand bath and heated by a Bunsen burner.

One hundred cc toluene, 175 cc Oettel solution, diffused light, boiling temperature, anode in toluene:

Total silver chloride	= 21.4500 grams.
Side chain silver chloride	= 9.6105 grams.
Total chlorine	= 5.3200 grams.
Six hours $\times$ 2 amperes	= 12.0 amp. hrs.
Twelve ampere hours equivalent to	= 15.86 grams Cl.
Chlorine available	= 7.93 grams.
Efficiency	= 66.9 percent.
Percentage ring	= 55.3 percent.
Percentage chain	= 44.7 percent.

Experiment 5.—In this experiment three electric light carbons bunched together were used for anodes and platinum for cathode.

Seventy-five cc of toluene and 175 cc of Oettel solution were electrolyzed at boiling temperature in very diffused light.

Total silver chloride	= 2.4757 grams.
Side chain silver chloride	= 0.7035 gram.
Ring silver chloride	= 1.7722 grams.
Total chlorine	= 0.6140 gram.
Six hours $\times$ 2 amperes	= 12.0 amp. hrs.
12 ampere hours equivalent to	= 15.86 grams Cl.
Chlorine available	= 7.93 grams.
Efficiency	= 7.73 percent.
Percentage ring	= 71.55 percent.
Percentage chain	= 28.45 percent.

Experiment 6.—This experiment is identical with Experiment 5, except that it was carried out in absolute darkness.

Total silver chloride	= 1.9987 grams.
Side chain silver chloride	= 0.450 gram.
Ring silver chloride	= 1.5487 grams.
Total chlorine	= 0.495 gram.
Six hours $\times$ 2 amperes	= 12.0 amp. hrs.
Twelve ampere hours equivalent to	= 15.86 grams Cl.
Chlorine available	= 7.93 grams.
Efficiency	= 6.22 percent.
Percentage chain	= 22.6 percent.

In this and the experiment preceding, the carbon anode suffered considerable disintegration, the entire solution being filled with powdered carbon and the bottom of the flask was covered with a layer of it. The chlorine at the anode may have attacked the binding material of the carbon instead of substituting in the toluene, thus accounting for the low efficiency in Experiments 5 and 6.

Experiment 7.—Graphite block was substituted for the gas carbon as anode.

Seventy-five cc of toluene, 175 cc of Oettel solution, diffused light:

Total silver chloride	= 14.3295 grams.
Side chain silver chloride	= 6.0367 grams.
Ring silver chloride	= 8.2928 grams.
Total chlorine	= 3.54 grams.
Six hours $\times$ 2 amperes	= 12.0 amp. hrs.
Twelve ampere hours equivalent to	= 15.86 grams Cl.
Chlorine available	= 7.93 grams.
Efficiency	= 44.50 percent.
Percentage ring	= 57.8 percent.
Percentage chain	= 42.2 percent.

Experiment 8.—The above experiment was repeated with conditions identical except that all light was excluded.

Total silver chloride	= 12.0885 grams.
Side chain silver chloride	= 5.0767 grams.
Ring silver chloride	= 7.0118 grams.
Total chlorine	= 2.995 grams.
Six hours $\times$ 2 amperes	= 12 amp. hrs.
Twelve ampere hours equivalent to	= 15.86 grams Cl.
Chlorine available	= 7.93 grams.
Efficiency	= 37.7 percent.
Percentage ring	= 58.2 percent.
Percentage chain	= 41.8 percent.

From the above results it is seen that there is very little difference between *darkness* and *very diffused light*, at least so far as the percentage ring and chain substitution is concerned. What difference there is, is in the right direction, for a higher percentage of side chain chlorine is expected in the light than

in darkness from the results obtained in the ordinary chlorination of boiling toluene in sunlight.

Experiment 9.—In this experiment the arrangement was the same as that used in Experiment 4, except that concentrated hydrochloric acid was substituted for the Oettel solution.

Seventy-five cc of toluene and 100 cc of concentrated hydrochloric acid, platinum anode, boiling temperature.

Total silver chloride	= 7.8495 grams.
Side chain silver chloride	= 1.1692 grams.
Ring silver chloride	= 6.7403 grams.
Total chlorine	= 1.9850 grams.
Six hours $\times$ 2 amperes	= 12.0 amp. hrs.
Twelve ampere hours equivalent to	= 15.86 grams Cl.
Chlorine available	= 7.93 grams.
Efficiency	= 25.00 percent.
Percentage ring	= 85.85 percent.
Percentage chain	= 14.15 percent.

In this experiment the platinum anode was dissolved and after four hours a gas carbon electrode was substituted. This electrode was disintegrated to some extent.

Experiment 10.—In this and the next experiment the conditions were identical with Experiments 7 and 8, except that concentrated hydrochloric acid was substituted for the Oettel solution.

Seventy-five cc of toluene, 100 cc of concentrated hydrochloric acid, diffused light, boiling toluene, graphite anode.

Total silver chloride	= 16.2097 grams.
Side chain silver chloride	= 5.7000 grams.
Ring silver chloride	= 10.5097 grams.
Total chlorine	= 4.02 grams.
Six hours $\times$ 2 amperes	= 12.0 amp. hrs.
Twelve ampere hours equivalent to	= 15.86 grams Cl.
Chlorine available	= 7.93 grams.
Efficiency	= 50.5 percent.
Percentage ring	= 64.8 percent.
Percentage chain	= 35.2 percent.

Experiment 11.—This is identical with the above experiment except that all light was excluded.

Total silver chloride	= 22.4512 grams.
Side chain silver chloride	= 6.7177 grams.
Ring silver chloride	= 15.7335 grams.
Total chlorine	= 5.57 grams.
Six hours $\times$ 2 amperes	= 12.0 amp. hrs.
Twelve ampere hours equivalent to	= 15.86 grams Cl.
Chlorine available	= 7.93 grams.
Efficiency	= 70.0 percent.
Percentage ring	= 70.2 percent.
Percentage chain	= 29.8 percent.

Experiment 12.—Ninety cc of toluene and 120 cc of concentrated hydrochloric acid were electrolyzed with direct current in a pear-shaped flask between vertical carbon electrodes of one-half inch diameter set about one and one-half inches apart and extending to the bottom of the flask. This flask was connected with a return condenser and heated on a sand bath to the boiling temperature of the liquid. The experiment was conducted in very diffused light.

Total silver chloride	= 20.4192 grams.
Side chain silver chloride	= 6.4854 grams.
Ring silver chloride	= 13.9338 grams.
Total chlorine	= 5.07 grams.
Six hours $\times$ 2 amperes	= 12.0 amp. hrs.
Twelve ampere hours equivalent to	= 15.86 grams Cl.
Chlorine available	= 7.93 grams.
Efficiency	= 63.9 percent.
Percentage ring	= 68.2 percent.
Percentage chain	= 31.8 percent.

Experiment 13.—Twenty-five grams of cold toluene were treated drop by drop with 6 grams of lead tetrachloride. Hydrochloric acid gas was evolved and could be detected by the odor. The toluene turned a beautiful red color, lasting several hours, but which finally disappeared, leaving the solution clear with a precipitate of white lead chloride in the bottom of the beaker. Some white precipitate was formed, together with the red color on adding the lead tetrachloride to the toluene. If the lead tetrachloride is added too fast, the reaction tends to become violent and the solution spatters.

On analysis the following results were obtained:

Total silver chloride	= 0.9225 gram.
Side chain silver chloride	= 0.0 gram.
Total chlorine	= 0.229 gram.
Available chlorine (6 grams PbCl_4)	= 0.61 gram.
Efficiency	= 37.5 percent.

This experiment is analogous to that of benzene and lead tetrachloride.

Experiment 14.—Sixty-five cc. of toluene and twelve grams of anhydrous ferric chloride were placed in a round bottom flask, fitted with a return condenser and a thermometer, the bulb of which dipped into the toluene. This was placed in bright sunlight and slightly warmed from time to time. A brisk reaction took place beginning at 45° and varying from that to 60° . The odor of hydrochloric acid was very noticeable at the top of the condenser. After four hours, the flask was cooled and the liquid decanted off and filtered, giving a deep brownish black oil.

Analysis of 5 cc portion gave:

Total silver chloride	= 0.2861 grams.
Side chain silver chloride	= 0.0116 gram.
Percentage ring	= 95.5 percent.
Percentage side chain	= 4.5 percent.

The brown oil gave a blue color (Turnbull's blue) with potassium ferricyanide, thus showing the presence of ferrous iron.

The methods used in analyzing the products of the chlorination of toluene were as follows:

The total chlorine was determined with alcohol and sodium according to the method of Stephanow mentioned before. Usually five or ten cc of chlorinated toluene were added to 50 cc of alcohol. This was placed in a round bottom flask, fitted with a return condenser, and heated to boiling on the water bath. Sodium was then dropped into the solution, piece by piece, through the return condenser. A great excess of sodium was used, probably twenty-five times that required by theory. The heating was continued over a couple of hours and the liquid in the flask changed to a very viscous

semi-solid condition. There was always some metallic sodium left at the end of a heating. After cooling, water was carefully added till the whole mass dissolved to a brownish yellow liquid; then dilute nitric acid and silver nitrate. Some tests on known amounts of chlorine substitution products showed this method to possess a very fair degree of accuracy when properly carried out.

Chlorine in the side chain was determined by prolonged boiling with alcoholic silver nitrate. The first precipitate of silver chloride was filtered off on a Gooch filter, the liquid then boiled again and the precipitate again removed and so on until no more silver chloride came down. This method also checked up very well when run with a known sample.

To get the addition chlorine, the filtrate from the above side chain determination was boiled with alcoholic caustic, then acidified with dilute nitric acid and excess of silver nitrate added. This is the same procedure that is used for benzene hexachloride.

Looking over the results obtained it is seen that at low temperatures and fairly high current density, the total efficiency is very low.

The experiments check quite well in regard to the percentage chain and ring substitution. There seems to be very little difference between very diffused light and absolute darkness.

The results obtained in Experiment 3 are of particular interest in that an extremely low current density was used. As a result it is seen that substitution takes place almost entirely in the ring, and also the efficiency is much higher than in the first two experiments with a higher current density.

The ordinary chemical method of getting chlorine into the ring with a compound such as toluene is to use a carrier and pass in chlorine with the toluene at a low temperature and in the dark. Evidently in Experiment 3 these results have been duplicated in a very satisfactory manner with the electric current. The work of a carrier has been duplicated electrolytically.

In the electrolytic chlorination of boiling toluene using the Oettel solution as a source of chlorine it is seen that the percentage of chlorine in the ring is about double that obtained at the temperature of melting ice with a corresponding current density (on account of the disintegration suffered by the carbon anode in Experiments 5 and 6, the results obtained therein will be disregarded for the present). Also the efficiency is much better, and as before there is very little difference in the results with very diffused light and absolute darkness.

Ordinarily, if chlorine is passed into boiling toluene, especially in the sunlight, substitution takes place largely in the side chain. On passing chlorine into boiling toluene, in ordinary diffused light, Cohen¹ obtained a result of ten percent to twenty percent in the ring, and ninety to eighty percent in the side chain.

Therefore, in the electrolytic chlorination of boiling toluene, it would be expected that a combination of these results and the effect of a carrier would be obtained, since it has already been found that electrolytic chlorine was similar to that obtained in the presence of a carrier. This is, in fact, what happens, as the results show a combination of the two effects and the amount of chlorine in the side chain is within a few percent of that in the ring.

In the experiments carried out by Cohen¹ on the electrolytic chlorination of boiling toluene results are obtained which differ from those found in this work, in that the chlorine goes into the ring to the entire exclusion of the side chain. Since he used a slightly different apparatus and concentrated hydrochloric acid as a source of chlorine it was thought that possibly this might account for the discrepancy between his results and those obtained in this work. Therefore, concentrated hydrochloric acid was substituted for the Oettel solution in the apparatus used in the preceding experiments and several runs were made.

¹ Cohen-Dawson-Crosland: Jour. Chem. Soc., 87, 1034 (1905).

In the first of these, Experiment 9, the platinum anode was destroyed and the gas carbon substituted for it was largely disintegrated so that the experiment was repeated, using a graphite anode, which was found to suffer practically no disintegration. The results show a fairly good efficiency of chlorination and a slightly higher percentage of side chain chlorine in diffused light than in darkness. This was also noticed with the Oettel solution and is what should be expected. Although the side chain chlorine with the hydrochloric acid is about ten percent less than with the Oettel solution, it still amounts to a good percentage of the total chlorine substituted and by no means duplicates the results obtained by Cohen.

In looking around for the possible reasons for this discrepancy it was thought that the responsibility might be fixed on the different arrangement of the electrodes in the two cases. In these experiments the cathode was immersed in and exposed only to the liquid used as a source of chlorine. Correspondingly, the anode was exposed to come in contact, only with the toluene. In Cohen's apparatus the electrode consisted of two carbon rods in an upright position both extending down through the layer of toluene well into the liquid used as a source of chlorine.

Therefore, in Experiment 12 an apparatus was fixed up which resembled very closely that used by Cohen. The amounts of toluene, hydrochloric acid, and the current used were identical with amounts used by him. The results obtained agree very well with those in Experiments 10 and 11 in which the original apparatus was used. Thus, the discrepancy in results is not due to the form of the apparatus used. Therefore, the only possible reason for the difference in results would seem to be in the time over which the electrolysis was extended.

Cohen makes no statement as to the duration of the run nor as to the efficiency, but, judging from the quantity of chlorinated toluene obtained by him, the run must have extended over a considerably longer period than the time of

these experiments, *i. e.*, six hours. This prolonged boiling introduces the possibility that the side chain chlorine first obtained was completely hydrolyzed, and on continued electrolysis practically all finally substituted in the ring. Again, unless he obtained an efficiency of one hundred percent, which is quite improbable, it is hard to see why any chlorine not substituted, but set free, would not go into the side chain as it would in the ordinary chlorination of boiling toluene with gaseous chlorine.

The theories and discussion given under the chlorination of benzene can be applied equally well to the chlorination of toluene. With toluene as with benzene, the hydrogen of the ring may be considered as negative in character. The side chain hydrogen of toluene may be considered as positive. Then, negative chlorine will displace ring hydrogen and positive chlorine, the hydrogen of the side chain.

It is known that if chlorine be passed in cold toluene in the presence of a carrier and very diffused light, substitution takes place in the ring almost entirely. Here, negative chlorine from the ferric chloride displaces negative hydrogen just as in the case of benzene. Under the same conditions of temperature and diffused light, electrolytic chlorine, which may be considered as negative, substitutes largely in the ring, especially at low current densities. Chlorine set free from an instable compound such as lead tetrachloride substitutes in the ring and not in the side chain. If lead tetrachloride be considered as breaking down according to the following equation,



it is seen that the negative chlorine displaces the hydrogen of the ring just as in the corresponding case with benzene.

Again, the chlorine set free when toluene is treated with ferric chloride alone substitutes almost entirely in the ring, fully in accordance with the theory and parallel to the action with benzene. Thus, it is seen that electrolytic chlorine reacts toward toluene in the dark and at low temperature in a manner entirely analogous to ordinary chlorine in the pres-

ence of a carrier, or chlorine from instable chlor compounds. If ordinary gaseous chlorine is passed into boiling toluene in sunlight, substitution takes place almost entirely in the side chain. It may be considered that, at boiling temperature and in the light, dissociation of ordinary chlorine gas takes place into positive and negative chlorine. The positive chlorine may then displace the positive hydrogen of the side chain of the toluene, forming benzyl chloride. The hydrogen may unite with the negative chlorine and form hydrogen chloride.

In the electrolytic chlorination of toluene the efficiency at the higher temperature is several times as good as that obtained at lower temperatures, under similar conditions as to current density. The high side chain substitution in this case is probably due to the chlorine which had heretofore escaped as chlorine gas now substituting directly in the side chain in the same manner as ordinary chlorine at the higher temperature. This accounts for the higher efficiency obtained with boiling toluene than with cold toluene.

The chlorination of toluene was next studied under conditions similar to those necessary for the formation of addition products when applied to benzene. Toluene was chlorinated in the presence of dilute alkali, dilute acid and water.

Experiment 15.—One hundred cc of toluene and 75 cc of one percent sodium hydroxide solution were placed in a gas wash bottle and chlorine gas bubbled through for one and one-half hours,—very diffused light. The oil was then washed fifteen or twenty times with water in a separatory funnel or till no turbidity with silver chloride was observed in the wash water after the same had been standing in contact with the oil for some time. Ten cc portions were then removed for analysis.

The total chlorine was determined with sodium and alcohol according to the method previously described. The side chain chlorine was determined by boiling with alcoholic silver nitrate. The filtrate from this was treated with alco-

holic caustic soda and boiled for some time, acidifying with dilute nitric acid and precipitating with silver nitrate.

In the case of benzene this treatment gives half of the addition chlorine, the other half substituting in the ring. With toluene this may give half, or perhaps some other fraction of the total addition chlorine, depending on how much substitution there has been previous to this treatment.

In any case it furnishes a means for comparing the relative amounts of addition chlorine obtained in a series of experiments with toluene, all performed under practically the same conditions. The substituted ring chlorine is, of course, obtained by difference.

In tabulating these experiments, the addition chlorine is put down as obtained by precipitation, and then for the sake of comparison, these results are multiplied by 2 as would be done in the case of benzene addition products. Percentage ring chlorine is obtained by taking twice the addition chlorine precipitated and adding to it the side chain chlorine and then subtracting this from 100.

One hundred cc toluene and 75 cc of one percent sodium hydroxide solution were placed in a gas wash-bottle and chlorinated for one and one-half hours,—diffused light, room temperature. There was a slight rise in temperature and the oil turned a yellow color.

Analysis of 10 cc.

Total silver chloride	= 2.1081 grams.
Side chain silver chloride	= 0.6312 gram.
Addition silver chloride	= 0.4580 gram.
Percentage side chain	= 30.0 percent.
Percentage addition precipitated	= 21.75 percent.
Twice percentage addition precipitated	= 43.50 percent.
Percentage ring by difference	= 26.5 percent.

Experiment 16.—Same as in the preceding except that water was substituted for the caustic soda solution.

Total silver chloride	= 1.3823 grams.
Side chain silver chloride	= 0.3110 gram.
Addition silver chloride	= 0.3195 gram.
Percentage side chain	= 22.55 percent.
Percentage addition precipitated	= 23.15 percent.
Twice percentage addition precipitated	= 46.30 percent.
Ring percentage, by difference	= 31.15 percent.

Experiment 17.—This experiment is identical with Experiment 15 except that a one percent hydrochloric acid solution was substituted for the caustic soda solution.

Total silver chloride	= 1.3708 grams.
Side chain silver chloride	= 0.3528 gram.
Additional silver chloride	= 0.3832 gram.
Percentage side chain	= 25.75 percent.
Percentage addition precipitated	= 27.95 percent.
Twice percentage addition precipitated	= 55.90 percent.
Ring percentage, by difference	= 18.35 percent.

Experiment 18.—This experiment is identical with Experiment 15 except that it was carried out in absolute darkness.

Total silver chloride	= 1.4505 grams.
Side chain silver chloride	= 0.3412 gram.
Additional silver chloride	= 0.3182 gram.
Percentage side chain	= 23.5 percent.
Percentage addition precipitated	= 21.9 percent.
Twice percentage addition precipitated	= 43.8 percent.
Ring percentage, by difference	= 32.7 percent.

Electrolysis of Sulphuric Acid—Insoluble Sulphur

It¹ has been shown that light will change sulphur which is dissolved and therefore soluble in carbon bisulphide into a modification which is insoluble in this solvent. Berthelot² has shown that when sulphuric acid is electrolyzed at high current density, sulphur is deposited at the cathode. He found this sulphur to be amorphous and insoluble in carbon disulphide. Heat changed it into the soluble variety. Berthelot obtained but very small quantities of this sulphur.

¹ Ranklin: Jour. Phys. Chem., 11, 1 (1907).

² Berthelot: Ann. Chim. Phys. [3], 49, 488 (1857).

Electrolysis of Sulphuric Acid

The following experiments were carried out under varying conditions of temperature, and the percentage of sulphur soluble in carbon disulphide was determined.

Experiment 1.—Concentrated sulphuric acid in a small beaker was electrolyzed between a platinum anode and a lead cathode (5 cm x 1 cm) at high current density (3 amperes), using a porous cup and keeping the beaker packed in ice. The temperature of the acid did not exceed 40°. About one-half of a gram of sulphur was obtained of which 65 per cent was insoluble in carbon disulphide.

Experiment 2.—The run was repeated at a temperature of about 100° and practically all the sulphur was found to be soluble in carbon disulphide. Evidently by electrolysis some insoluble sulphur is formed provided the temperature be kept low. Of course, at a higher temperature this would be changed over to the soluble modification. Since it has been shown that light will change the soluble modification of sulphur over to the insoluble modification, and that by the electrolysis of sulphuric acid insoluble sulphur is obtained at the cathode, it is of interest to note that evidently there must be an analogy between the two processes by which this insoluble sulphur is produced, since the product of each process is the same.

Herschel's Work

In the Philosophical Transactions of the Royal Society for the year 1842 (page 201) is found a paper by J. F. W. Herschel describing the action of the solar spectrum on papers which had been impregnated with various substances more or less sensitive to light.

Herschel found that paper which had been washed in a solution of ferric chloride or ammonio-citrate of iron and potassium ferricyanide, thereby giving it a brownish green color, would, on exposure to light, become covered with a layer of Prussian blue. If the action of light be continued, the blue is replaced by white, which, in turn, takes on a

brownish violet hue. He says that the whitening is obviously due to the de-oxidation of the precipitated Prussian blue and to the formation of the proto-ferrocyanuret of iron.

A number of experiments were performed for the purpose of duplicating these results electrolytically.

Experiment 1.—Filter paper or good "linen" paper was moistened with a solution of ferric chloride and potassium ferricyanide, giving it a light yellowish brown color. This was placed on a glass plate and two platinum strip electrodes brought into contact with it at a distance of about 3 cm from each other, and held down by suitable weights. On passing about 0.521 milliampere between these electrodes for a short time, a deep blue color is found under the cathode. The anode is either unchanged or turned slightly brown. On further electrolysis the cathode space turns white, and on still further electrolysis, this white changes to a brown color which is permanent. These reduction effects obtained under the cathode correspond exactly to the effects obtained by Herschel when he exposed paper similarly prepared to the action of sunlight. It is thus possible to make a series of electrolytic and solar prints which resemble each other very closely.

For instance, any desired figure, say the letter "C" can be cut out of a sheet of copper, and after being carefully polished, laid on a sheet of paper which has been impregnated with a solution made up of ferric chloride and potassium ferricyanide. Under this paper is a sheet of wet blotting paper, which, in turn, rests on a sheet of metal, that serves as the anode, the metallic "C" being the cathode. Using a low current density a blue "C" is very soon obtained which, after the paper has been washed with an excess of water, is permanent and resembles, in all respects, an ordinary blue print. The reaction takes place so quickly in this experiment that it is possible to write or draw pictures in blue, by simply using the end of the cathode wire as a pen and going over the paper prepared and arranged as above, in

the same manner and at the same speed that would ordinarily be used with pen and ink.

Other light-sensitive papers were treated in this manner. Ordinary silver or "solio" paper was impressed with an electrolytic "C," the copper cathode having been plated with silver. After toning in the usual gold solution this "C" comes out a deep reddish brown color, exactly similar to a solar print.

Paper was treated with starch and allowed to dry. A solution of lead acetate was then poured over this starch paper and allowed to dry. The paper was then dipped in a strong solution of potassium iodide which caused the paper to take on a yellow color, due to the lead iodide formed. This sensitized paper was impressed with an electrolytic "C" which, after the paper had been allowed to remain in a strong solution of ammonium chloride, came out in a purple color due to the iodine set free. This is entirely analogous to the behavior of this paper in the sunlight.¹ From these results it is seen that the action of sunlight is similar to electrolytic reduction and *vice versa*. In other words, it is a case of actinic electrolysis.

Herschel describes further experiments in which paper was washed with a solution of ammonio-citrate of iron and exposed to light for different periods of time, and then treated with potassium ferricyanide. A sample of paper thus prepared was exposed for four or five seconds to sunlight. On bathing this in potassium ferricyanide solution a good Prussian blue color was obtained.

Another sample of paper so prepared was exposed for a very long time to the solar spectrum. When this paper was bathed in the potassium ferricyanide solution a most intense blue color was developed over the more refrangible region, in the interior of which the blue color appears to have been, as it were, eaten away, leaving a white oval; precisely the same phenomenon which would have been produced under the

¹ Eder: Handbuch der Photographie, IV (4).

spectrum had the two liquids acted in conjunction. Herschel has thus shown that light first reduces ammonioferric citrate and then converts it into a reducing agent.

From these experiments it would seem that light reduces the iron of the ammonioferric citrate to the ferrous condition so that it gives a blue color with potassium ferricyanide, and at the same time oxidation of the ammonium citrate takes place with the consequent formation of a reducing agent. This reducing agent then acts on the potassium ferricyanide and reduces it to potassium ferrocyanide. A colorless compound is then obtained, which is the ferrous ferrocyanide or the proto-ferrocyanuret of iron mentioned by Herschel.

The following experiments were performed in order to determine whether it was possible by electrolytic oxidation to convert ammonium citrate into a reducing agent:

Reduction Through Oxidation

A solution of ammonium citrate was electrolyzed between platinum electrodes, at moderate current density, a porous cup being used. Silver nitrate was added to the anode compartment. After a few minutes the solution in the anode compartment darkened and a fine black precipitate came down. This can be shown to be metallic silver: by grinding in a mortar, also by dissolving in nitric acid and precipitating with hydrochloric acid. This shows that ammonium citrate can, by oxidation, be converted into a reducing agent and affords a further instance of the electrolytic duplication of photo-chemical reactions.

In a further attempt to get a reducing agent through oxidation, bromine was slowly added to alcohol in the sunlight. A vigorous reaction took place and the odor of acetaldehyde was very noticeable. However, the liquid remained red in color and evidently there was some bromine and hydrobromic acid present for, on adding silver nitrate, a yellow-white precipitate of silver bromide came down. If any of the silver nitrate had been reduced to silver, this white pre-

precipitate completely masked it, as no metallic silver could be detected. Alcoholic silver nitrate was treated with bromine, but no better results were obtained.

Lecture Room Experiments

FURTHER EXPERIMENTS ON THE REDUCING ACTION OF LIGHT

Experiment 1.—A solution of ferric chloride and oxalic acid was added to a solution of potassium ferricyanide. This was diluted to a clear light yellow solution. A portion of this exposed to sunlight, burning magnesium ribbon, or arc light, turned blue almost at once. This indicates the reduction of ferric chloride to ferrous chloride and the subsequent formation with the potassium ferricyanide present of Turnbull's blue.

Experiment 2.—A few cubic centimeters of water were placed in a test tube and on this a layer of toluene. A few drops of bromine were then added and the whole shaken thoroughly, thus imparting a red color to the toluene. When this was exposed to a strong source of light, such as a burning magnesium ribbon, the toluene became colorless at once, thus showing the accelerating effect of light on the reaction between bromine and toluene.

Photo-Electric Experiments

ACTION OF LIGHT ON SILVER BROMIDE AND PLATINUM BLACK ELECTRODES IN VARIOUS ELECTROLYTES

Experiment 1.—Silver plates were covered with a layer of the bromide by making them anode in a solution of hydrobromic acid.

Two of these silver bromide electrodes were carefully washed and suspended in a solution of potassium bromide contained in a glass dish. The electrodes were connected to a sensitive low resistance galvanometer of the d'Arsonval type. A mirror was arranged so as to reflect a beam of sunlight on either one or both of the electrodes. If both electrodes were illuminated at once, the galvanometer moved

either one way or the other as it was almost impossible to get the electrodes of exactly the same size and value.

On illuminating the electrodes separately it is found that which ever one is illuminated becomes the positive pole of the cell or the cathode.

Experiment 2.—If one electrode be dipped into a solution of erythrosine for a moment and then withdrawn and the excess of dye removed before the electrode is returned to the original potassium bromide cell, then on illumination of both electrodes the *undyed* electrode becomes cathode,—the dyed electrode being anode. If the undyed electrode is then dyed and replaced in the solution and both electrodes illuminated as before, the freshly dyed electrode is anode. And so the process can be repeated a great many times; in each case, the freshly dyed electrode is anode.

Experiment 3.—With platinum black electrodes in two beakers joined by an inverted U-tube, the illuminated dyed electrode becomes cathode,—just the reverse of the above effect. No effect was obtained with the electrodes undyed.

Experiments in photo-electricity have been carried out by many workers, including Becquerel, Minchin, Wilderman and others.

Minchin¹ covered silver plates with a layer of silver bromide and used two of them as electrodes in a solution of potassium bromide. He found that the electrode exposed to light became cathode. This result was duplicated in Experiment 1. The light seems to cause a reduction of the silver bromide, perhaps to a sub-bromide or finally to metallic silver. The bromine then is set free at or reacts with the electrode in the dark, *i. e.*, the anode.

Wilderman² repeated many of Minchin's experiments and studied some of them with much care. He found that the current always flowed from the electrode in the dark to the one in the light and that the cell was constant and non-polarizable so long as the film of silver halide on the cathode

¹ Minchin: Phil. Mag. [5], 31, 208 (1891).

² Wilderman: Phil. Trans., 206A, 335 (1906).

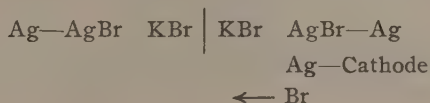
had not been reduced to silver. When the cathode had been reduced to silver the cell became inconstant and polarized. By changing the cathode to the halogen compound again, the cell was completely restored. Wilderman thus explains the results of Minchin and the action of the cell in a satisfactory manner, but does not explain the results obtained when a sensitizer was used in the cell.

Minchin coated a silver plate with eosine and gelatine. On exposure to light he found that this plate became cathode in the cell. In another experiment he immersed two clean silver plates in a solution of eosine. In this case the plate exposed to the light became anode for a moment and then reversed to cathode. Wilderman has suggested that his reversal is due to polarization. The natural direction of the current is that first shown.

An experiment of considerable interest which Minchin performed was to immerse two silver bromide electrodes into a solution of potassium bromide and connect this cell with a source of electricity. The anode was visibly blackened by the passage of the current, but the cathode showed no visible change. However, on placing the cathode in pyrogallol developer it darkened in a manner similar to an ordinary exposed plate. There would seem to be a close analogy to the process taking place at the cathode and that which takes place on exposure to light.

It would seem that the effects obtained in the preceding experiments may be obtained as follows:

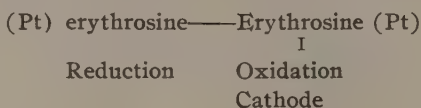
In Experiment 1 with two silver bromide electrodes in potassium bromide solution and one electrode illuminated, metallic silver is set free from the bromide at the illuminated electrode, making it cathode and the halogen travels as ion to the other electrode where it reacts to form more silver bromide.



In Experiment 2 the dyed electrode becomes anode. Since it has been shown that by the action of light on sensitizers halogen is set free; in this case the halogen may react with the electrode forming silver halide and thus causing the electrode to become anode. Light acting on the undyed electrode, as in the preceding experiment, would tend to cause it to become cathode, thus adding to the effect produced at the dyed electrode. This double effect is, in a measure, opposed by the tendency of light to act on the silver halide of the dyed electrode and to precipitate silver in a manner similar to that on the undyed. However, the double effect mentioned above will always be greater than this and thus cause the dyed electrode to become anode.

Of course, when two silver bromide electrodes of the same size are illuminated, there is a tendency to precipitate silver on each electrode or, in other words, each electrode tends to become cathode, and they exactly oppose each other. Thus the E. M. F. due to the action of the halogen from the sensitizer would be that which would determine the direction of the current as is shown above.

In Experiment 3, with electrodes of platinum black, the dyed electrode becomes cathode. This effect is similar to that obtained by Minchin. This may be explained by the fact that light acting on erythrosine would tend to set the halogen free as in the preceding experiment. The halogen, in this case iodine, cannot react with the platinum electrodes as it did with the silver one in Experiment 2, so that in this case the action is an oxidizing one and the cell becomes an oxidation reduction cell.



From Minchin's experiment it is seen that reduction of silver halide at the cathode of an electrolytic cell will affect it in a manner similar to the action of light. In the same

way in Experiment 1 it is seen that light acting on a silver halide electrode, generates an E. M. F. which sets up a current, indicating that at the electrode in question a reduction process is taking place. The E. M. F. generated by the action of light on sensitizers is in agreement with the fact that halogen is set free from them by the reaction of light.

These results do not throw any light on the action of sensitizers in a photographic plate. In the photographic plate the gelatine acts as a chemical sensitizer taking up halogen from the erythrosine, this latter then taking up halogen from the silver halide. The erythrosine thus acts as a halogen carrier. In the electromotive force experiments, there was nothing to absorb the halogen set free from the erythrosine and the direction of the current, therefore, depended on the reaction of the halogen.

Fluorescence

A series of experiments were carried out with the object of studying the chemistry of the reaction which takes place in fluorescent substances during exposure to light. In order to determine whether the fluorescence of various compounds was due to oxidation or reduction by light, these compounds were subjected to both chemical and electrolytic oxidation and reduction.

Experiment 1.—Uranium nitrate—water solution—also dilute nitric acid and dilute sulphuric acid solutions, 15 grams salt to 100 cc. of water were electrolyzed between platinum electrodes at varying current densities up to two amperes. The solutions were reduced to a green color but no fluorescence appeared. On being oxidized again with nitric acid in the dark no luminescence was observable.

Solutions of 20 grams of uranium salt in 100 cc of fifty percent sulphuric acid and also in ten percent nitric acid were electrolyzed between platinum electrodes in darkness at varying current densities, both alternating and direct, but no luminescence was observed.

Oxidation by Chemical Means

A solution of quinine sulphate in dilute sulphuric acid which had a good blue fluorescence was treated with solid sodium peroxide. The reaction went slowly at first and gradually increased in vigor. In a perfectly dark room it was possible to observe a well-defined greenish yellow luminescence, the intensity of which was proportional to the vigor of the reaction. With too great concentration of the sulphuric acid, the reaction went too fast and the luminescence was not apparent.

A number of blank experiments were run in dilute sulphuric acid without the quinine sulphate being present, but no luminescence was observed. The presence of the quinine therefore seems to be necessary for obtaining the effect. Sodium peroxide was added to cold water and the solution poured into quinine sulphate solution in the dark but no effect was observed. The same luminescence was observed when sodium peroxide was added to a dilute nitric acid solution of uranium nitrate.

Alkaline and acid solutions of eosine and fluorescein were treated in the same way without any results.

The best results were obtained with a fairly strong solution of quinine sulphate, not too acid, with sulphuric acid. This has a beautiful blue fluorescence in sunlight. On dropping a few grams of the powdered sodium peroxide into the quinine solution the reaction does not start at once, but only after five or ten seconds, and gradually increases in vigor, at the same time causing a luminescence which extends down into the solution and over an area of about 4 square centimeters. This experiment can hardly be taken to mean that the emission of fluorescent light is due to oxidation, since the effect seems to be obtained only when the solid salt acts on the solution and not when a solution of the sodium peroxide is poured into the quinine sulphate. The above solutions were each electrolyzed between platinum electrodes with direct current in a dark room but no luminescence could be observed.

FLUORESCENT SALTS IN SOLUTION TREATED WITH VARIOUS
OXIDIZING AGENTS—PERSULPHATES

Quinine, uranium, fluoresceine, eosine, were each treated in turn with such oxidizing agents as sodium persulphate, ammonium persulphate, potassium persulphate and sodium perborate. The experiments were performed in a dark room, however, no luminescence was observable. The three persulphates did not decompose very rapidly. Manganous sulphate was added and while it seemed to cause more rapid decomposition of the persulphates, yet no luminescence was observed. The sodium perborate gives off oxygen quite readily, but causes no luminescence. It was first thought that, by direct oxidation or reduction of the fluorescent substance, luminescence might be obtained. Since this did not appear to be borne out by experiment, the possibility presented itself that certain rays might be evolved during the reaction of an oxidizing agent, which would excite a fluorescent body to luminescence. It was thought that perhaps when such oxidizing agents acted directly on solutions of fluorescent salts the fluorescent properties might have been destroyed. Thus, it would have been impossible to detect any luminescence which might have resulted from the rays evolved during the oxidizing action of the persulphates.

To overcome this difficulty the oxidation was carried out inside a quartz bulb tube, which was immersed in a fluorescent solution. The bulb tube was partially filled with dilute sulphuric acid and to this the solid persulphate was added. Thus the oxidation process was entirely separated from the fluorescent solution and still any rays of ultra-violet light which might be evolved could have access to the fluorescent solution.

Several experiments were performed, using this apparatus and adding various persulphates to the acid in the tube, however, no luminescence was observed in any case.

Several electrolytic experiments were carried out with this same quartz tube. It was partially filled with dilute

sulphuric acid and into this two lead wire electrodes were immersed. The quartz tube was then suspended in a beaker of fluorescent solution. Thus in case any rays of an ultra-violet nature or rays which could in any way affect a fluorescent solution were emitted during oxidation or reduction processes at the electrodes, they would have a chance to act on the fluorescent solution. The fluorescent solution, not being subjected to electrolytic oxidation or reduction, would remain unchanged and its fluorescent properties would be unimpaired.

When the lead electrodes were connected to alternating current, luminescence was observed. It was found that the luminescence was at the electrodes themselves and did not in any way depend on the fluorescence of the solution surrounding the quartz bulb.

Therefore, in the experiments described below, the quartz bulb was not immersed in the fluorescent solution.

Experiment.—Very dilute sulphuric acid was electrolyzed in a dark room with lead wire electrodes and alternating current,—60 cycles, 3 amperes, 2 amperes, and 1 ampere. Both electrodes take on a pale greenish yellow luminescence. The solution fills up with a fine white precipitate—lead sulphate—which obscures the electrodes, but by diffusing the light causes the whole solution to glow. The appearance of the luminescence is coincident with the passage of the current and seems to depend on the intensity of the current as three amperes gave a better effect than one ampere. Also the greater the current density, the quicker the solution fills up with the white precipitate. The lead electrodes were replaced with platinum wires, but no luminescence was observed. This also precludes the possibility of the luminescence having been caused by a static discharge between the electrodes. With lead electrodes and direct current the luminescence was not observed. The anode becomes covered, almost immediately, with a layer of brown lead peroxide, and the solution does not fill up with the white precipitate. During electrolysis of the dilute acid with alternating current the lead electrodes were dissolved at a fairly rapid rate.

Electrolysis of Fluoresceine

A solution of fluoresceine weakly alkaline with sodium hydroxide was electrolyzed between platinum strip electrodes with porous cup, two amperes, direct current, temperature 25° and 50°. Apparently more gas comes off from the cathode than the anode. The cathode solution where filled with gas seems to take on a brick-red tinge, and on turning off the current, the red color slowly disappears and with it the gas held in suspension in the solution. This entire effect may be due to the gas held in suspension in the solution. After a while the cathode solution becomes lighter in color. Two samples, one from the anode and one from the cathode, if allowed to stand exposed to the air, tend to assume a common color. In the anode compartment the tendency is to deepen the color, if anything, but not the fluorescence. Eosine behaves much the same way.

After running some time the cathode solution is pretty well bleached out retaining a very slight pink color and fluorescence. After electrolyzing, to this extent, the anode solution is deepened in color and samples removed from each compartment and allowed to remain exposed to the air, do not assume their original color within any reasonable time. However, it is doubtful whether these experiments prove anything, as no fluorescence is destroyed nor is any fluorescence created or increased in intensity. Nor is the color on reduction changed to a green or yellow fluorescent shade as the case may be. The cathode effect can be duplicated by taking some of the original solution and diluting with water.

If a solution of eosine is treated with sodium peroxide a practically colorless solution results. This solution was treated with dilute nitric acid, then with silver nitrate and the amount of precipitated silver bromide determined.

	$C_{20}H_6Br_4O_5$ eosine (hot)	Eosine (cold)	Sodium salt eosine (cold)
Weight sample.....	0.2823	0.2398	0.1679
AgBr precipitated.....	0.2518	0.2206	0.1146
100 % bromine as AgBr..	0.3275	0.2785	0.1828
Percent bromine precipi- tated.....	76.8	79.2	62.6

From these results it is evident that a large part of the bromine in eosine is set free on treatment with sodium peroxide, *i. e.*, on oxidation.

The experiment was next tried of treating eosine and erythrosine with a reducing agent such as hydrogen evolved from zinc dust and sodium hydroxide. The solution of the dye is quickly changed to a colorless solution without any fluorescence. As before, these solutions were tested for the amount of halogen set free. Temperature = 25°.

	Eosine	Erythrosine
Weight sample	0.1507	0.0944
AgBr or AgI precipitated.....	0.0261	0.0259
100 % halogen salt.....	0.1746	0.1065
Percent halogen precipitated	14.95	24.3

From these results it is seen that some halogen is set free on the reduction of eosine or erythrosine.

Eosine, erythrosine or fluorescein can be reduced to a colorless solution with zinc dust in sodium hydroxide. On exposure to sunlight this solution immediately changes to a colored fluorescent solution. A sample of any one of the above which has been reduced to a colorless solution with zinc and sodium hydroxide will not change to a colored solution on standing in the dark, at least within a space of twenty-four hours.

A solution of erythrosine in water does not fluoresce to an appreciable extent. If the colorless solution, obtained by the reduction of an erythrosine solution, is placed in the sunlight, it takes on a pink color together with a green fluorescence. This will also take place in a tightly stoppered bottle with all air excluded, though in this case, the red color precedes the fluorescence. If some of the colorless solution be diluted and allowed to stand in a beaker in the sunlight for some time the solution takes on a beautiful greenish colored fluorescence much resembling fluoresceine. Thus, a non-fluorescent liquid is changed to a fluorescent one.

Eosine behaves in practically the same way except that it is, of course, fluorescent before reduction. However, the final fluorescence obtained after exposure of the reduced solution to sunlight more resembles fluorescein than eosine.

Fluoresceine behaves exactly as the two solutions mentioned above.

From the preceding experiments it is seen that the fluorescence of a solution can be destroyed by oxidation or reduction. In the case of reduction the effect of light is to restore the fluorescence.

The foregoing experiments would seem to indicate that the fluorescence of a substance is not due to a simple oxidation or reduction but evidently consists of a reaction of more complicated nature.

Action of Sunlight on Sensitizers

Erythrosine and Water.—Two solutions of different concentrations were made up and portions of each placed in two small glass stoppered bottles with as little air present as possible. One set of bottles was placed in sunlight and the other set in the dark. The more dilute solution of erythrosine bleached in a few hours in the sunlight and the other one bleached after a couple of days. The solution in the dark remained unchanged. Filter paper dyed with erythrosine and exposed to light bleached after a few hours. Porous porcelain plates dyed with erythrosine bleached after a few days.

The solution which had been bleached in sunlight gave a small amount of white precipitate with silver nitrate.

A solution of erythrosine, water and potassium arsenite, was made up and placed in glass stoppered bottles, and one sample exposed to sunlight and the other placed in the dark, as in the preceding case. In the sunlight the solution quickly takes on a light brown color with a green fluorescence. The samples in the dark remains unchanged. An alcoholic solution of eosine bleaches very slowly in sunlight.

A solution of erythrosine, water and sodium sulphite

changes to a light yellowish brown with a green fluorescence when exposed to sunlight. In darkness there is no change.

A solution of erythrosine, water, sodium hydroxide and sodium sulphite gives a deep red solution with green fluorescence when exposed to sunlight. When compared with a sample which has been allowed to remain in the dark it is found that the red color has deepened considerably in the sunlight. The solution in the dark has not changed.

A solution of erythrosine, water and sodium thiosulphate, also the same solution with sodium hydroxide added, both changed to a deep red color in sunlight without any fluorescence. In the dark there is no change.

The above experiments on the action of light on organic dyes in the presence of reducing agents were prompted by the work of E. Vogel.¹ He treated solutions of erythrosine with hydroxylamine hydrochloride and sodium hydroxide, with sodium hydroxide alone, and also with hydrogen peroxide. A portion of each solution was exposed to sunlight and the other portion kept in the dark. After a short exposure to sunlight the solutions had changed as follows:

The hydrogen peroxide solution showed no visible change.

Sodium hydroxide solution had bleached a little.

The neutral solution had bleached a little.

The solution containing hydroxylamine was entirely changed; the tetraiodfluoresceine had been reduced to ordinary fluoresceine.

Vogel found that all the bromine and iodine substituted eosine dyes behaved like erythrosine. The experiments cited in this paper confirm the work of Vogel.

Reducing agents such as sodium arsenite and sodium sulphite when mixed with erythrosine and exposed to light caused the reduction to take place very quickly. The experiments show conclusively that organic dye stuffs can be reduced by light.

Potassium permanganate added to solutions of eosine

¹ Vogel: Wied. Ann., 43, 462 (1891).

and erythrosine exposed to sunlight for several days give a flocculent brown precipitate in the bottom of the beaker and a clear supernatant liquid. This clear liquid gives a precipitate with silver nitrate showing that some halogen has been set free.

Several glass plates were coated with gelatine, dyed with erythrosine and exposed to sunlight for several weeks, one-half of each plate being carefully protected from the light.

On some of the plates the dye was made slightly alkaline with ammonia and others had small amounts of ammonium bromide present with and without ammonium hydroxide. A set of these plates was exposed to the sunlight, in a suitable glass bottle filled with hydrogen, thus eliminating any effect which the oxygen of the air might have on the dye.

Abney exposed a gelatine plate dyed with cyanine to the light, then coated it with silver bromide emulsion in the dark and succeeded in developing the plate. The object of the above experiments was to duplicate the results of Abney, using the sensitizer erythrosine instead of cyanine. In all cases the part of the plate exposed to the light bleached after several weeks of exposure. Some plates were given an exposure of only a few hours.

The plates containing ammonium bromide were immersed for a few minutes in a bath of silver nitrate which, of course, precipitated silver bromide in the gelatine. They were then developed in a slow developer but no difference in the two halves of the plate could be detected. The plates which did not contain the ammonium bromide, were first immersed in a bath of either ammonium or potassium bromide, then in silver nitrate and developed as before. The results were equally unsatisfactory.

From the results of these experiments it is seen that when light acts on a sensitizer, such as erythrosine, it bleaches it and sets free some halogen. When the sensitizer is in the presence of a reducing agent, such as sodium sulphite or arsenite the clear red solution of erythrosine takes on an appearance much resembling fluoresceine. This reaction takes

place so quickly that it can be performed as a lecture experiment by using an arc light or magnesium ribbon as a source of light. The reaction here seems to be the same as that described in a preceding experiment where the erythrosine was reduced to a colorless solution with zinc and sodium hydroxide and afterwards, on exposure to light, took on a color and fluorescence resembling fluoresceine. Halogen was also set free in this case.

When a sensitizer is oxidized halogen is set free, though with a strong oxidizing agent like potassium permanganate it is probable that decomposition takes place.

Summary

The general results of this paper are:

(1) The rate of the reaction between ferric sulphate and copper is dependent on the rate of diffusion of the liquid. Ordinary means of measurement do not show the reaction to be of a photo-chemical nature.

(2) The electrolytic chlorination of acetic acid is unsatisfactory. Electrolytic chlorine is different in character from that due to the dissociating influence of sunlight on ordinary chlorine.

(3) The electrolytic chlorination of benzene is satisfactory from a standpoint of efficiency. The chlorine obtained by electrolysis is similar in action to ordinary chlorine in the presence of carriers such as ferric chloride, at low temperature and in diffused light or darkness.

(4) Chlorine from such instable compounds as lead tetrachloride acts in a manner similar to electrolytic chlorine, displacing the hydrogen of the benzene ring.

(5) Benzene can be chlorinated by the direct action of ferric chloride, provided the two are heated together and exposed to sunlight.

(6) Experimental facts in the chlorination of benzene in the presence of a carrier indicate a displacement of the hydrogen of the ring by the halogen and subsequent forma-

tion of hydrogen halide. Facts are opposed to the formation of addition compounds between the benzene and the carrier.

(7) With toluene, chlorine obtained electrolytically, or from instable compounds such as lead tetrachloride or from ferric chloride, substitutes in the ring at low temperatures. At higher temperatures electrolytic chlorine also substitutes in the side chain.

(8) Sulphur obtained by the electrolysis of sulphuric acid is similar to that precipitated from a solvent by the action of light.

(9) Many of the photo-chemical experiments of Herschel have been duplicated electrolytically.

(10) It has been shown that, by oxidation, ammonium ferric citrate can be converted into a reducing agent.

(11) In the cases studied, fluorescence is not the result of a simple chemical oxidation or reduction, but is apparently due to a more complicated reaction.

(12) In the electrolysis of dilute sulphuric acid with alternating current and lead electrodes a luminescence is obtained extending over each electrode.

(13) The action of solid sodium peroxide on a solution of quinine sulphate is accompanied by a luminescence.

(14) Photo-electric experiments show that light tends to set halogen free from a sensitizer.

(15) If a sensitizer, such as eosine or erythrosine, be reduced and allowed to stand in sunlight it is converted into a fluorescent substance.

(16) If a sensitizer, such as eosine or erythrosine, be exposed to light in the presence of a reducing agent it is very quickly converted into a fluorescent substance.

(17) Experiments show that organic dyes can be reduced by light.

(18) The results obtained in this work agree with and tend to confirm the Grotthuss theory of the action of light.

This work was suggested by Professor Bancroft and carried out under his direction.

The author takes this occasion to express his apprecia-

tion of the many suggestions received from Professor Bancroft and of his very generous interest in the work.

Thanks are also extended to Professor Orndorff and to Dr. Delbridge of the Department of Organic Chemistry for interest taken in the work and for the use of materials belonging to that department.

